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EXAMINATION OF COTTRELL DUST FROM THE COPPER SMELTER OF KIDD CREEK MINES LIMITED, TIMMINS, ONTARIO

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EXAMINATION OF COTTRELL DUST FROM THE COPPER SMELTER OF KIDD CREEK MINES LIMITED TIMMINS, ONTARIO

by

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ABSTRACT

Kidd Creek Mines Limited currently is trying to recycle Cottrell dust from their copper smelter to their adjacent zinc plant. Under certain conditions, this practice gives rise to both high Fe^{2+} levels in the zinc processing solutions and premature precipitation and subsequent loss of silver as a jarosite-type compound. The Cottrell dust supplied for examination by the company consists principally of $PbSO_4$, $CuSO_4.5H_2O$, $ZnO.Fe_2O_3$, $ZnSO_4.H_2O$, $(Cu,Fe)SO_4.H_2O$ and quartz, together with many minor or trace constituents including copper oxides (Cu_2O and CuO), copper sulphides and metallic copper. Virtually all the iron in the dust is present in the trivalent state. During leaching in acidified ferric sulphate media typical of zinc plant solutions, the copper sulphates and zinc sulphates are readily leached. The copper oxides and copper are also dissolved and the copper sulphides are partly leached; this results in the concomitant reduction of much of the dissolved ferric ion to the ferrous state. Traces of potassium and sodium are also dissolved, but the amounts

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do not seem adequate, by themselves, to cause premature precipitation of Ag-bearing jarosite in the zinc plant. Some possible causes for this premature precipitation of jarosite that include increased potassium loading, the presence of excess $PbSO_4$, pH effects and the addition of seed particles are discussed.

EXAMEN DE LA POUSSIÈRE DE COTTRELL PROVENANT DE LA FONDERIE DE CUIVRE DE KIDD CREEK MINES LIMITED À TIMMINS (ONTARIO)

par

J.E. Dutrizac* et T.T. Chen*

RÉSUMÉ

La Kidd Creek Mines Limited essaie actuellement de recycler la poussière de Cottrell provenant de sa fonderie de cuivre dans son usine de zinc adjacente. Dans certaines conditions, cette pratique entraîne des concentrations en Fe^{2+} élevées dans les solutions de zinc ainsi qu'une précipitation prématurée et une perte subséquente d'argent sous forme de composé de type jarosite. La poussière de Cottrell fournie par l'entreprise à des fins d'examen est composée principalement de $PbSO_4$, $CuSO_4.5H_2O$, $ZnO.Fe_2O_3$, $ZnSO_4.H_2O$, $(Cu,Fe)SO_4.H_2O$ et de quartz. Elle contient aussi des traces d'oxydes de cuivre (Cu_2O et CuO), de sulfures de cuivre et de cuivre métallique. Pratiquement tout le fer est présent à l'état trivalent. Pendant la lixiviation dans un milieu acidifié contenant du sulfate ferrique couramment rencontré dans les usines de zinc, les sulfates de cuivre et de zinc sont facilement lixiviés. Les oxydes de cuivre et le cuivre sont aussi dissous et les sulfures de cuivre sont partiellement lixiviés; cela entraîne la réduction concomitante d'une grande partie des ions ferriques dissous en ions ferreux. Des traces de potassium et de sodium sont aussi dissoutes mais les quantités ne semblent pas suffisantes en elles-mêmes pour provoquer la précipitation prématurée de jarosite contenant de l'argent dans l'usine de zinc. On examine des causes possibles de cette précipitation prématurée de jarosite, comme une plus grande charge en potassium, un excès de $PbSO_4$, des effets du pH et l'addition de semences.

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INTRODUCTION

Kidd Creek Mines Limited operates both a copper smelter and a roast-leach-electrowin zinc plant at Timmins, Ontario. Continuing efforts are being made to integrate the two operations to achieve a maximum overall recovery of both the major (Cu,Zn) and minor (Ag,Cd,Pb) elements. Within this framework, some 30 mt/d of Cottrell dust from the copper smelter is being recycled to the zinc plant to try to recover both the contained copper and zinc and to concentrate lead and silver into a suitable residue. Recent changes in copper smelting practice related to the degree of oxygen enrichment have, however, produced undesirable consequences in the zinc leaching circuit. Large quantities of ferrous ion were generated and premature formation of a Ag-bearing jarosite occurred. This premature precipitation resulted in a significant silver loss, and the formation of excess ferrous ion necessitated prolonged solution oxidation in subsequent iron removal stages.

Because CANMET is currently conducting both a detailed balance of the Kidd Creek zinc circuit and an in-depth investigation of jarosite formation, the problems caused by the Cottrell dust were considered to form part of the CANMET program. Accordingly, two samples of Cottrell dust from the Kidd Creek copper smelter were examined to investigate the causes of the premature jarosite precipitation and the reasons for the excessive ferrous ion formation.

EXPERIMENTAL

MATERIALS

Two samples of Cottrell dust from the Kidd Creek copper smelter were provided; these were designated as "June 9" and "June 20". Some analytical data were provided by the company and others were obtained at CANMET using conventional techniques. Efforts were made to determine the Fe^{2+}/Fe^{3+} ratio in the dusts using wet chemical methods (HCl dissolution under N_2), but numerous side reactions occurred that resulted in continuous changes in this ratio with time. The procedure was finally abandoned in favour of Mossbauer analysis.

MOSSBAUER SPECTROSCOPY

Both as received samples were examined for Fe^{2+} and Fe^{3+} on a conventional constant acceleration Mossbauer spectrophotometer operating in transmission geometry with a laser interferometer for velocity calibration. The γ-ray source consisted of Co^{57} in a rhodium matrix. Its intensity was approximately 80 mCi. Each spectrum consisted of many hundreds of points and was interpreted using a standard computer program.

LEACHING STUDIES

The two samples of Cottrell dust were leached both in water and in 6 g/L Fe^{3+} - 50 g/L H_2SO_4 media. The leaching was done in air for 1 h at 30°C using 25 g of dust in 250 mL of solution; these conditions were selected to approximate those likely to be used in commercial practice. After leaching, the slurries were filtered with the filtrate being brought to volume for analysis. The solids were then washed, dried at 30°C and examined.

X-RAY DIFFRACTION

The solids before and after leaching were analyzed by standard Debye-Scherrer X-ray powder diffraction methods to identify the major phases present.

MICROSCOPIC EXAMINATION

Polished sections of the dusts, before and after leaching, were prepared, and were examined using conventional light microscopy and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX). Unfortunately, many of the particles were <1 μm, and meaningful analyses could not be realized.

RESULTS AND DISCUSSION

CHEMICAL DATA

The analytical data obtained for the two Cottrell dust samples are presented in Table 1. The June 9 sample contains significantly more copper and less zinc than the June 20 material; in other respects the two dusts are reasonably similar. Most of the sulphur is present as sulphate. Lead sulphate and copper sulphate were detected by X-ray diffraction as was readily soluble zinc sulphate. The alkali concentrations are modest. A significant amount of arsenic is present, but antimony is virtually absent.

THE VALENCE STATE OF IRON IN THE DUSTS

Mossbauer study of the dusts indicated that virtually all the iron was present in the Fe^{3+} form which would be expected considering the highly oxidizing nature of the copper smelting procedures employed at Kidd Creek

Table 1. Chemical Analysis of the June 9 and June 20 Copper Cottrell Dusts

Element	June 9 Sample		June 20 Sample	
	Kidd Creek	CANMET	Kidd Creek	CANMET
Cu	18.1%	-	12.9%	-
Fe	6.5%	5.9%	5.15%	4.35%
Zn	19.8%	-	23.0%	-
S_{Total}	11.0%	-	11.3%	-
$S^o + S^{2-}$	1.34%	-	0.44%	-
Pb	7.5%	-	8.7%	-
Na	-	0.05%	-	0.04%
K	-	0.13%	-	0.12%
As	-	0.87%	-	1.0%
Sb	-	<0.02%	-	<0.02%
Ag	-	544 ppm	-	286 ppm

Mines. A quadrupole split, 2-line spectrum was obtained for each sample and similar isomer shifts were observed as shown below.

June 9 Sample	June 20 Sample
0.219 mm/s	0.209 mm/s
0.204 mm/s	0.220 mm/s

These isomer shift values are characteristic of ferric ion (0-0.5 mm/s); values in excess of 0.5 mm/s are expected for ferrous ion. A relatively smooth baseline was realized, suggesting the nearly total absence of Fe^{2+}. Both the June 9 and June 20 dusts yielded very similar spectra.

The absence of Fe^{2+} in the original dusts indicates that the troublesome ferrous ion is being formed by the reduction of dissolved ferric ion by various components in the dust. As will be seen later, the dusts contain minor amounts of copper oxides, copper sulphides and copper. It is suggested that these react with the acidic ferric sulphate media to generate the ferrous ion.

$$Cu_2O + 2Fe^{3+} + 2H^+ \longrightarrow 2Cu^{2+} + 2Fe^{2+} + H_2O \quad (1)$$

$$Cu_2S + 2Fe^{3+} \longrightarrow CuS + 2Fe^{2+} + Cu^{2+} \quad (2)$$

$$CuS + 2Fe^{3+} \longrightarrow Cu^{2+} + 2Fe^{2+} + S^{o} \quad (3)$$

$$Cu^{o} + 2Fe^{3+} \longrightarrow Cu^{2+} + 2Fe^{2+} \quad (4)$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \quad (5)$$

MINERALOGICAL CHARACTERIZATION OF THE DUSTS

X-ray diffraction analysis of the two dust samples revealed them to be similar with the following phases being identified: $PbSO_4$, $CuSO_4.5H_2O$,

$ZnO.Fe_2O_3$, $ZnSO_4.H_2O$, $(Cu,Fe)SO_4.H_2O$, quartz, and trace amounts of Cu_2O and CuO. In addition, many other phases were present in trace amounts but could not be conclusively identified by X-ray diffraction methods.

Microscopically, the dusts are similar to those observed previously from other copper smelters (1) in that they consist of coarse spheres (solidified drops) of oxides, sulphides, etc. surrounded by much finer dust or fume particles. Figure 1 shows a typical field of view of the June 9 dust sample that illustrates the large spheres set amid much finer particles presumably consisting of lead sulphate, copper sulphate, zinc sulphate and various Fe-Zn-Cu oxides and silicates. The finer particles are often <1 μm and cannot be accurately analyzed. The spheres are, however, large enough for detailed study, and these were found to consist of a variety of phases as the following discussion indicates.

Metallic copper is present both as the principal component of some spheres and as inclusions in spheres composed predominatly of other copper compounds. Figure 2 shows a bright sphere of metallic copper rimmed by a ∿4 μm thick layer of Fe-Cu-Zn oxides (grey with light inclusions). The metallic copper spheres are often rimmed with oxides. The nebulous light grey aura surrounding the oxide rim seems to be zinc sulphate. Figure 3 shows a copper inclusion (white, right) in a sphere consisting of exsolved two-phase oxides. Sometimes, the copper and copper oxide phases are present in roughly equal amounts as illustrated in Figure 4 which shows a sphere of metallic copper (white) intergrown with copper oxide (light grey, likely Cu_2O). Regardless of its mode of occurrence, the metallic copper appears to be of high purity.

A large proportion of the spheres consist of copper oxide or Cu-Fe-Ca oxides, often co-existing as complex intergrowths. Figure 3 illustrates

such a complex oxide grain consisting of an intergrowth of copper oxide (white and likely Cu_2O) and Cu-Fe-Ca oxide (light grey). Occasionally, the second oxide phase also contains traces of Zn, Pb and S. Although these trace elements seem to be dissolved in the oxide, the presence of very fine inclusions cannot be entirely discounted. Spheres consisting of Cu_2O rimmed by CuO were observed, as were spheres of Fe-Zn oxide and Fe oxide containing traces of Zn, Cu and Ca. The various oxide phases tend to form the body of the spheres although they are also commonly present as rims or inclusions (Figure 5).

Several spheres consist essentially of copper sulphides which sometimes contain inclusions of iron oxides or Fe-Ca-silicates. The sulphide grains are occasionally rimmed with what appears to be a copper sulphate containing traces of Zn, Fe and Pb. Figure 5 illustrates two copper sulphide spheres (light grey) containing inclusions (dark grey) of Fe oxide and Fe-Cu-Zn-Ca oxides. As a general observation, the copper sulphide usually contains traces of Fe and Zn, and this fact may indicate that the sulphide is actually digenite, $Cu_{1.85}S$.

LEACHING OF THE DUSTS

Water leaching of the dusts resulted in negligible iron dissolution but significant copper solubilization (3.65 g/L in 250 mL, corresponding to ~20% Cu extraction). The water soluble copper likely reflects the leaching of hydrated copper sulphates; basic copper sulphates, copper oxides, etc. are not water soluble. The alkalis contained in the dusts also dissolved to the extent of 200 mg/L K and 70 mg/L Na in the original 250 mL of leaching medium. The measured extent of alkali dissolution

exceeds by 40-50% that analyzed in the original dusts. This likely reflects analytical problems associated with determining low levels of alkalis without contamination from the laboratory environment. The pH at the completion of the water leaching test (250 mL) was 4.6, indicating that few acid forming components are present in the dust itself.

When the acidic ferric sulphate medium was employed to leach the dusts, the ferric ion reacted with some of the constituents present (Equations 1-4) and, moreover, a modest net dissolution of iron occurred. The June 9 dust, which has a significantly higher Cu concentration, was slightly more reactive than the June 20 product as the data below indicate.

	June 9 Sample	June 20 Sample
Initial Fe^{3+}	5942 mg/L	5942 mg/L
Final Fe^{3+}	0 mg/L	1490 mg/L
Final Fe^{2+}	6686 mg/L	5027 mg/L
Net Fe Dissolution	744 mg/L	575 mg/L

Since the solution volume used for the above analyses was 500 mL, the weight (and % of total) of iron leached was 372 mg (∿25%) for the June 9 sample and 288 mg (∿26%) for the June 20 material. About 77% of the copper contained in the June 9 sample was solubilized to yield a 14 g/L Cu concentration in the original 250 mL of solution. Alkali extractions were similar to those observed during water leaching with the analytical data again suggesting >100% K + Na dissolution. The final pH of the 250 mL leaching solution was 1.93. After filtration, the leach solution was heated to 95°C for ∿4 h; a trace of yellow-white precipitate formed and this was shown to be amorphous (silica?) and not a jarosite-type compound. Jarosite precipitation was not expected because of the low alkali concentration and the lack of ferric ion.

Copper is one of the major elements dissolved during leaching by either water or acidic ferric sulphate, and the high copper concentrations realized cannot be particularly desirable in the zinc circuit. Although some of the copper is certainly present as water soluble $CuSO_4.xH_2O$, much appears to originate from the ferric ion attack of Cu_2O, CuO, Cu_2S or metallic copper. These phases tend to occur as relatively coarse spherical particles which are likely recovered early in the dust collection train. It would be technically useful if these coarser particles could be isolated from the remainder of the dust and recycled directly to the smelting furnace. Also, this study did not examine the fate of halogens although these are certainly of great concern to the zinc plant. The dusts also contain arsenic (Table 1, Ref. 1), and the possibility exists for this element to be present both as As^{3+} and As^{5+}. The removal of arsenic present in both its valence states could prove difficult in subsequent processing steps.

CHARACTERIZATION OF THE DUSTS AFTER LEACHING

X-ray diffraction analysis of the June 9 dust after leaching for 1 h in both water and the acidic ferric sulphate medium indicated the following phases.

June 9 Sample	June 9 Sample
H_2O Leached	Fe^{3+}-H_2SO_4 Leached
$PbSO_4$, $ZnO.Fe_2O_3$	$PbSO_4$, $ZnO.Fe_2O_3$
$CuSO_4.xH_2O$	trace $Cu_{1.8}S$
trace $Cu_{1.8}S$	

The leaching processes have been effective in removing the zinc sulphates, copper sulphates, copper oxides, etc., but have not significantly altered the other major phases present

Microscopically, the leached dusts were somewhat different from the original samples in that some of the fine material appears to have been dissolved away and many of the coarser spheres show signs of alteration and/or partial dissolution. A general view of the acidic ferric sulphate leached June 9 dust is shown in Figure 6 which indicates a somewhat coarser texture with respect to the unleached material (Figure 1) and the partial attack of several of the larger grains. In some cases (lower center) the interior of a sphere has been completely dissolved leaving only its rim (see also Figure 7). The following changes seem to have occurred during the acidic ferric sulphate leach.

1 - Copper oxides have been completely dissolved, and this dissolution is likely responsible for the hollow grid spheres of copper sulphide or Fe-Ca-Cu oxides seen in the leached sample (Figure 7, left and lower center).

2 - The amount of metallic copper has been greatly reduced with only a few inclusions in copper sulphide being noted. Much of the copper was originally present in rimmed spheres (Figures 2,3,4) and its dissolution could account for many of the hollow spheres evident in the acid leached product (Figure 6, Figure 7 upper right).

3 - Copper sulphides are still plentiful as evident in Figure 7 (three large solid light grey spheres) and Figure 8 (two central solid light grey spheres). The copper sulphides appear to have been altered, however, and "covellite" is now present. Most of the copper sulphides contain minor Fe and some have traces of Zn as well. The compositions of the copper sulphides were not determined quantitatively.

4 - Iron oxides are still plentiful (Figure 8, medium grey crystal in upper central area), and these contain traces of Zn, Cu, Ca, Pb and Sn.

5 - Numerous grains of zinc ferrite sometimes containing traces of Sn, Cu or Pb are present (Figure 6, etched sphere above size bar; Figure 9, large structured spheres and blockly crystal at upper left). Clearly the low leaching temperature and/or low terminal acidity have prevented significant ferrite dissolution and this conclusion is supported by the low iron extraction during leaching.

6 - Much of the finer granular material evident in Figure 6 was shown to be $PbSO_4$ (white); the sulphates of zinc or copper have been dissolved.

PRACTICAL IMPLICATIONS

Although the recycle of Cottrell dust from a copper smelter into a zinc plant will involve many problems such as halogen levels, impurity loadings, arsenic buildup, etc., the two issues of concern for the present study were:

1 - The formation of excessive amounts of ferrous ion in the leaching circuit.

2 - The premature precipitation of jarosite in the zinc leaching circuit that results in a significant loss of silver and other values like lead.

Ferrous ion is not a major component of the dusts themselves, but seems to be generated in the leaching circuit by the reduction of ferric ion by copper oxides (Cu_2O), copper sulphides (2) and metallic copper contained in the dusts. Since ferric ion is always likely to be present in the leaching media, the resolution of this problem would have to involve either the prior removal of the reducing agents or a subsequent prolonged reoxidation of the leaching medium. The reducing agents tend to exist as the coarser dust particles, and some progress might be made by a more

careful segregation of the dust from the first banks of Cottrells and its recycle to the copper smelting furnace. Such segregation would also reduce the copper loading in the zinc plant with obvious economic advantages. If segregation is not possible, a preleach with H_2SO_4-oxidant (air, MnO_2, H_2O_2, etc.) to dissolve copper, copper sulphates, copper oxides and copper sulphides (as well as some zinc) might be considered. This would isolate much of the copper early in the process and could reduce the halogen input to the zinc plant.

No single cause of the premature precipitation of jarosite-type compounds is readily apparent and possibly several factors are involved. Although some K and Na are leached from the dusts, the amounts are probably inadequate, by themselves, to cause jarosite precipitation (3,4). At Kidd Creek, the zinc processing solutions always contain some sodium, and the addition of a few hundred mg/L (K + Na) will not change the total alkali concentration significantly. Potassium, however, is by far the strongest jarosite forming alkali (3), and its presence would greatly favour jarosite precipitation even at low temperatures. The transfer of potassium from the Cottrell dusts to the leaching circuit is likely one factor leading to early jarosite formation. The Cottrell dusts contain a major amount of $PbSO_4$ and this would also contribute to jarosite formation, especially at temperatures $\sim 95^{\circ}C$. Lead jarosite forms readily at $95^{\circ}C$ and its precipitation would cause the nearly quantitative incorporation of any soluble silver into the jarosite-type precipitate (5). Work in progress at CANMET has shown the presence of lead jarosite and alkali jarosites in both the neutral leach and hot acid leach residues, with the lead jarosite being the dominant species. The high concentration of $PbSO_4$ in the dusts would favour lead jarosite formation and, once formed, the lead jarosite could serve as a seed for alkali jarosite growth.

Because the Cottrell dusts contain acid consuming phases, the pH of the leaching solution will rise considerably and this will also favour jarosite precipitation. In this study, the pH at the end of the acid leach was 1.9, a value quite suitable for jarosite formation. Possibly the use of a higher acid concentration during the leaching stage would prevent premature jarosite precipitation. Lastly, it may be that one or more of the finely divided components in the dust serves as a nucleus for jarosite formation. The addition of large amounts of a seeding material with the dust would greatly accelerate jarosite precipitation, especially under marginal conditions such as would exist at low alkali concentrations.

CONCLUSIONS

The two Cottrell dusts from the copper smelter of Kidd Creek Mines Limited, Timmins, Ontario were similar and consisted of major $PbSO_4$, $CuSO_4.5H_2O$, $ZnO.Fe_2O_3$, $ZnSO_4.H_2O$, $(Cu,Fe)SO_4.H_2O$ and quartz, together with many minor constituents such as copper oxides, copper sulphides and metallic copper. The copper oxides and metallic copper, and to a lesser degree the copper sulphides, react rapidly with ferric ion to produce ferrous ion which creates problems in subsequent iron removal operations. The precise causes for the premature precipitation of jarosite in the zinc leaching circuit were not identified. Some factors which might contribute to early jarosite formation were, however, advanced and these include the addition of jarosite forming alkalis (K and Na), the heavy loading of $PbSO_4$, the adjustment of the pH into the jarosite forming range, and the possible provision of seed for jarosite nucleation.

ACKNOWLEDGEMENTS

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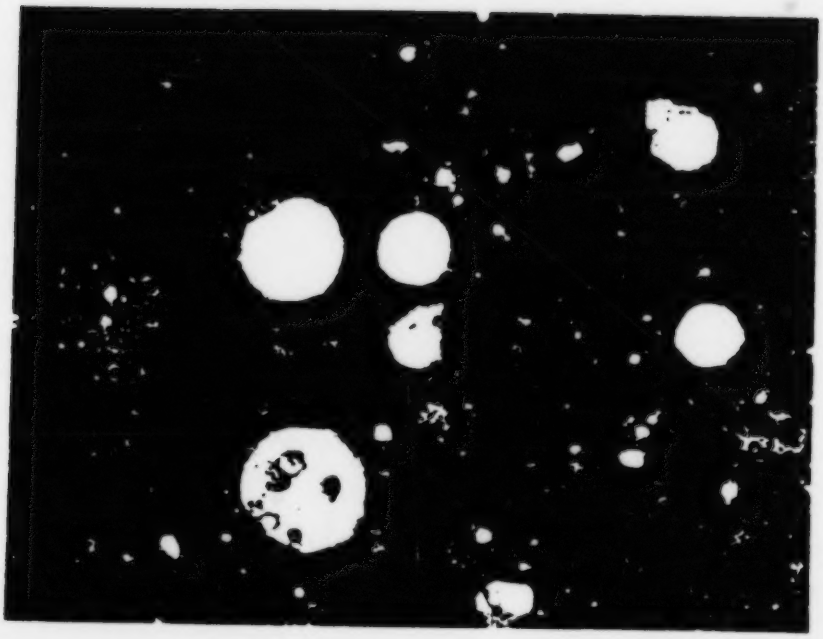

Fig. 1 - Typical field of view of the June 9 dust showing large spheres in a matrix of fine, irregular particles. (SEM backscattered electron photomicrograph.)

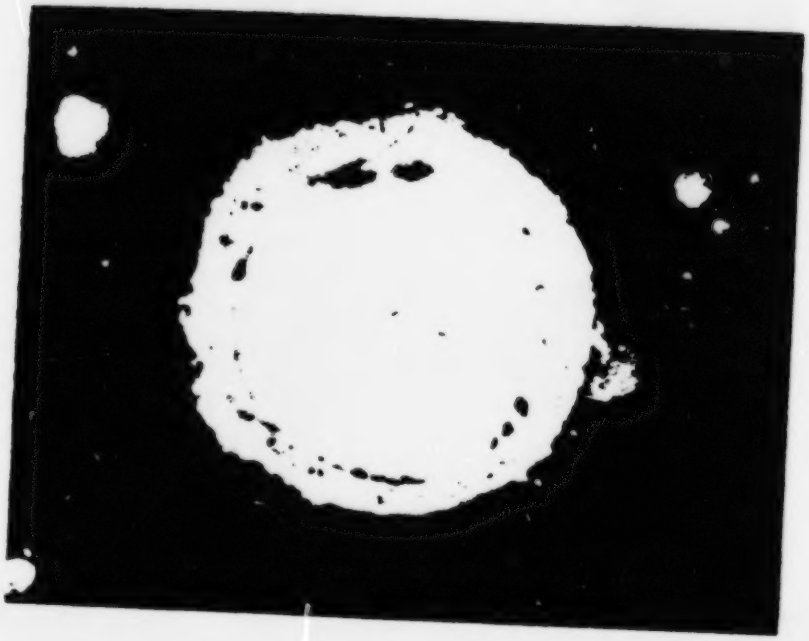

Fig. 2 - Rimmed sphere of metallic copper (white). (SEM backscattered electron photomicrograph.)

Fig. 3 - Inclusion of metallic copper (white) in sphere of two-phase oxides. (SEM backscattered electron photomicrograph.)

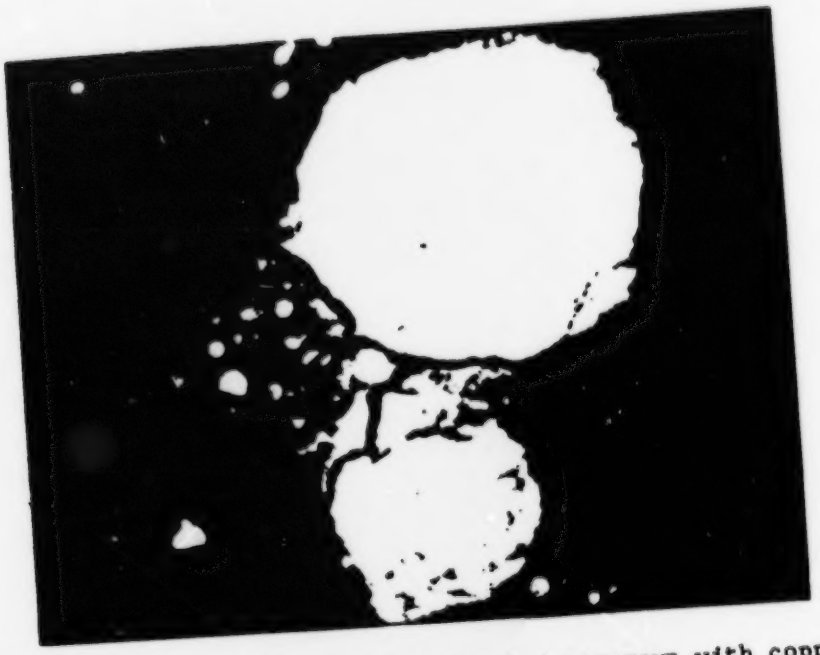

Fig. 4 - Sphere of metallic copper (white) intergrown with copper oxide (light grey). (SEM backscattered electron photomicrograph.)

Fig. 5 - Spheres of copper sulphide (light grey) containing inclusions (dark grey) of various iron oxides. (SEM backscattered electron photomicrograph.)

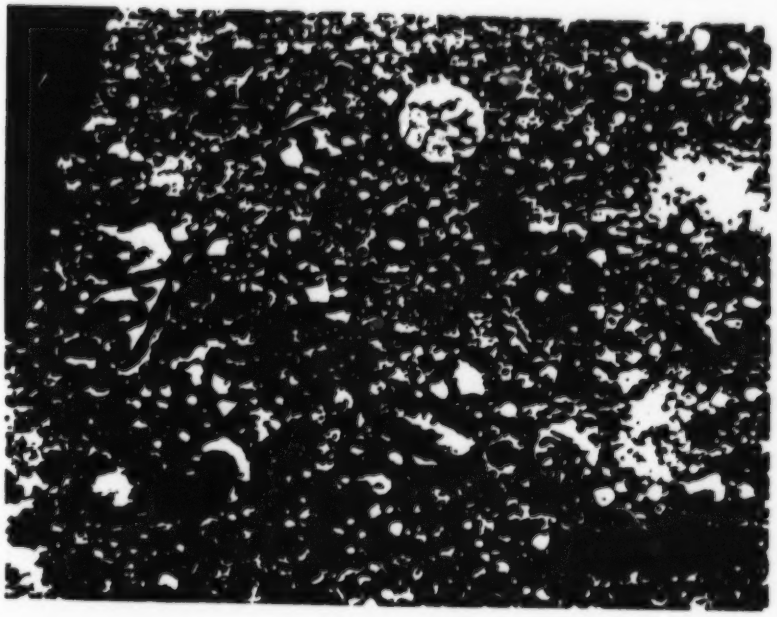

Fig. 6 - General view of the June 9 dust after leaching in Fe^{3+}-H_2SO_4 media. (SEM secondary electron photomicrograph.)

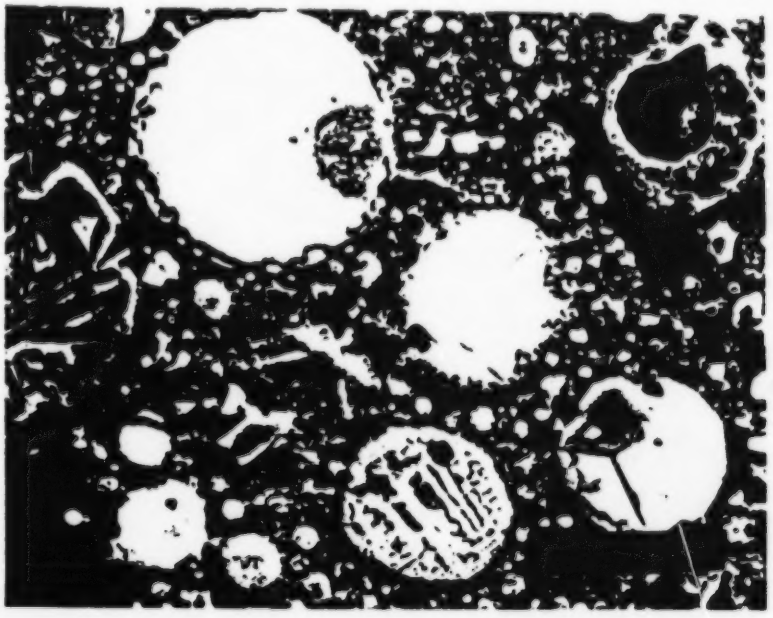

Fig. 7 - Hollow grid spheres illustrating the selective removal of copper oxides or copper from Fe or Fe-Ca-Cu oxides. (SEM secondary electron photomicrograph.)

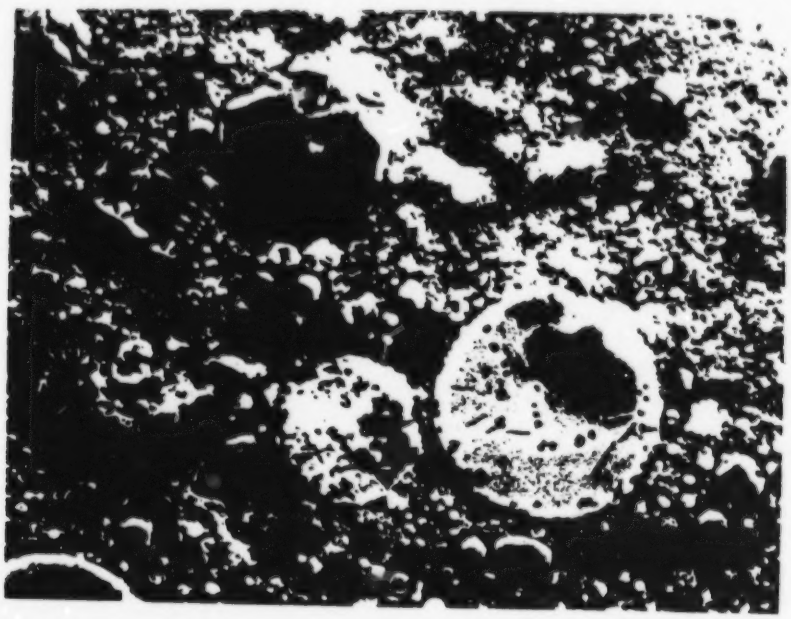

Fig. 8 - Two spheres of copper sulphide (lower center) and a crystal of Fe oxide containing traces of Cu, Zn and Ca (upper center). (SEM secondary electron photomicrograph.)

Fig. 9 - High resolution view showing fine spheres of zinc ferrite (white) together with blockly crystals of zinc ferrite or Zn-bearing iron oxides. (SEM secondary electron photomicrograph.)